

Electrochemical Oxidation of Tetrabutylammonium Salts of Aliphatic Carboxylic Acids in Acetonitrile

F. J. González-Bravo and Mónica Galicia-García

Departamento de Química del Centro de Investigación y Estudios Avanzados, Av. Instituto Politécnico Nacional 2508. C.P. 07360, Apdo. Postal 14-740, D. F., México

In the present work, a series of linear aliphatic carboxylates such as acetate, propionate, butyrate, valerate, and hexanoate, were studied. We are focused in analyze by using of cyclic voltammetry and preparative scale electrolysis the anodic oxidation process without the interference of the oxidation of the solvent. Such as in the case of previous works¹⁻³, it was possible by using tetrabutylammonium salts of carboxylic acids in acetonitrile. Glassy carbon was selected as material for the work electrode in order to minimize the effect of carboxylate adsorption observed on noble metals.

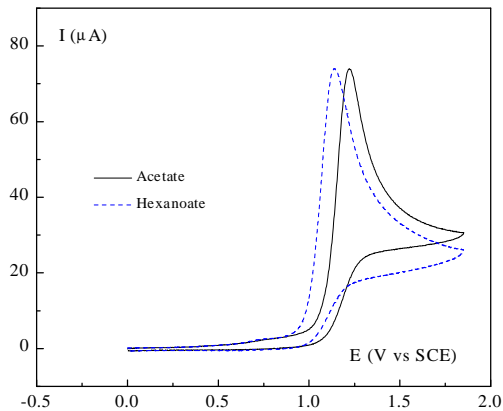


Figure 1. Cyclic voltammetry of tetrabutylammonium acetate and hexanoate 4 mM in acetonitrile + Bu₄NPF₆ 0.2 M on glassy carbon electrodes (ϕ = 3 mm) at 0.1 Vs⁻¹.

Figure 1 shows two typical cyclic voltammograms obtained for the acetate and hexanoate in acetonitrile on glassy carbon electrodes. The oxidation process is characterized by only one irreversible anodic peak. In the aliphatic series, it was observed that, the potential of oxidation is only moderately decreased with the increase of the aliphatic long chain. This behavior can be explained by the weak electron-releasing power of the alkyl substituents attached to the carbon α of the acetate ion. The diminution of the peak potential with the increase of the aliphatic long chain is furthermore compatible with the decrease of the gas-phase ionization potential (IP), which was obtained by geometry optimization from 6-31G* ab-initio calculations.

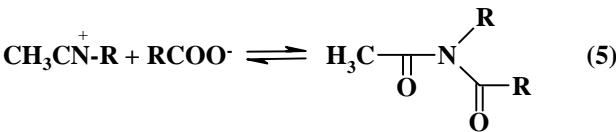
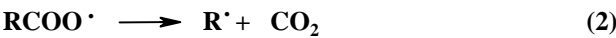
The voltammetric characterization of the mechanism of oxidation and decarboxylation was carried out by the analysis of the peak current, the peak potential and the half peak width as a function of the scan rate. We are focused to determine the stepwise or concerted nature of the oxidation and decarboxylation steps. In Table 1 is resumed the principal voltammetric characteristics used to determine the mechanism of electron transfer and decarboxylation. It can be observed that the average transfer coefficient α_{av}, calculated from the average half-peak width, is not quite different from the apparent transfer coefficient calculated from the slope ∂E_p/∂logv.

	∂E _p /∂Logv (mV/dec.)	α _{app}	E _p - E _{p/2} (mV)	α _{av}
Acetate	46.2	0.65	88	0.54
Propionate	46.1	0.65	109	0.44
Butyrate	48.8	0.61	98	0.49
Valerate	48.1	0.62	96	0.50
Hexanoate	47.9	0.63	94	0.51

Table 1. The anodic oxidation of tetrabutylammonium carboxylates (4 mM) on a glassy carbon electrode (3 mm ϕ) in acetonitrile. The scan rate range used is from 0.1 to 5 Vs⁻¹.

The transition from a mechanism controlled by a follow-up chemical reaction to a mechanism controlled by electron transfer is determined by both, a variation of ∂E_p/∂logv from 29.6 to 59.2 mV/dec. and a variation of E_p-E_{p/2} from 47.5 to 95 mV³⁻⁴. The experimental results showed in Table 1 are in an intermediate situation. Thus, we can propose that the mechanism of oxidation and decarboxylation is stepwise in all the cases (reactions 1 and 2).

The coulometric analysis of the oxidation process at constant potential shows that the overall mechanism is monoelectronic for all the carboxylates studied. The formation of acylamides as principal products of electrolysis is in accord with the intervention of alkyl carbocations, which can react with a nucleophilic solvent such as the acetonitrile used in this study. The mechanism explaining the formation of this type of compounds is depicted by the reactions (1-5). The overall stoichiometry is consistent with the monoelectronic character of the process.



In all the cases, the absence of dimerization products such as ethane, butane, hexane, and octane, allows us to confirm that the Kolbe reaction is not promoted in our experimental conditions.

References

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